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The response of polypyrrole–DBS electrochemical molecular motors to Na concentration: Analogies in cell biology

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ABSTRACT

Conducting polymers employed as film electrodes in aqueous electrolytes can be viewed as a combination of electrochemical molecular motors, counterions and water: the material mimics the intracellular matrix of a muscle cell. The oxidation of a molecular motor promotes opposing macroscopic variations in the film, exchanging anions (swelling) or exchanging cations (contraction). The literature shows that the energy consumed by polymeric materials exchanging anions adapts to the local physicochemical conditions. Here, the effect of varying the electrolyte (NaCl) concentration on the electrochemical reactions of polypyrrole-DBS films under successive square current waves is presented. The reactions drive the exchange of cations with the electrolyte. The changes in the consumed energy, or the material potential, depend on the electrolyte concentration according to the same equations developed for materials which exchange anions. The energy consumed adapts instantaneously to new chemical conditions, thus containing quantitative information about the local chemical energy conditions. In terms of biological applications, the results could indicate that, regardless of the anion or cation, the energy of any chemical/biochemical reaction involving molecular motors includes quantitative information on the changing chemical conditions. Part of this energy may originate at the dendrite/muscle interface, the neuronal signal translating this information to the brain. However, the driving force which originates this nerve pulse remains unclear at present.

1. Introduction

One of the most eagerly anticipated goals in engineering is the development of technological devices able to sense their own working conditions, as do haptic muscles in animals. Thus, during a muscular contraction a nerve pulse is generated, providing the brain with quantitative information on the chemical conditions in the muscle [1,2]. The driving force which originates this pulse remains unclear. Artificial replication of these dual sensing–actuating properties could herald the dawn of new multifunctional (sensing–motor) devices driven by chemical/electrochemical reactions [3].

Electroactive materials, such as graphene, carbon nanotubes and conducting polymers, can experience changes in conformation, acting as molecular motors [4,5], and macroscopic structural volumetric changes [6,7] driven by reversible reactions. Control of these reversible volume variations has led to the development of artificial muscles [8,9].

These materials have traditionally been used as inactive supporting electrodes for electroanalytical sensors designed to detect analytes dissolved in the electrolyte, adsorbed on the electrode [10] or reacting on an adsorbed catalyst [11,12] or enzyme [13]. An alternative new sensing paradigm is now emerging: these materials (conducting polymers [14–16], carbon nanotubes [17], graphene [18]) can be used as electroactive sensing electrodes to detect the chemical and physical conditions around them.

Up to now, the use of motor reactions to sense reaction conditions has been studied and described theoretically using materials that exchange anions during *p*-doping/*p*-dedoping processes [3,19–22], in particular in films of polypyrrole materials [23,24]. These films are composed of molecular motors (the polymer chains): cooperative actuation during oxidation generates inside the material the free volume required to host ions and solvent molecules from the electrolyte to balance both charge and osmotic pressure, with the result that the film swells.

When using films of polypyrrole-macroanions, the macroanions remain trapped in the film and the same polypyrrole electrochemical molecular motors destroy, by oxidation, the free volume. The film shrinks, expelling solvent molecules and cations to the electrolyte [25,26]. The transformation of the bonds caused by the reaction in

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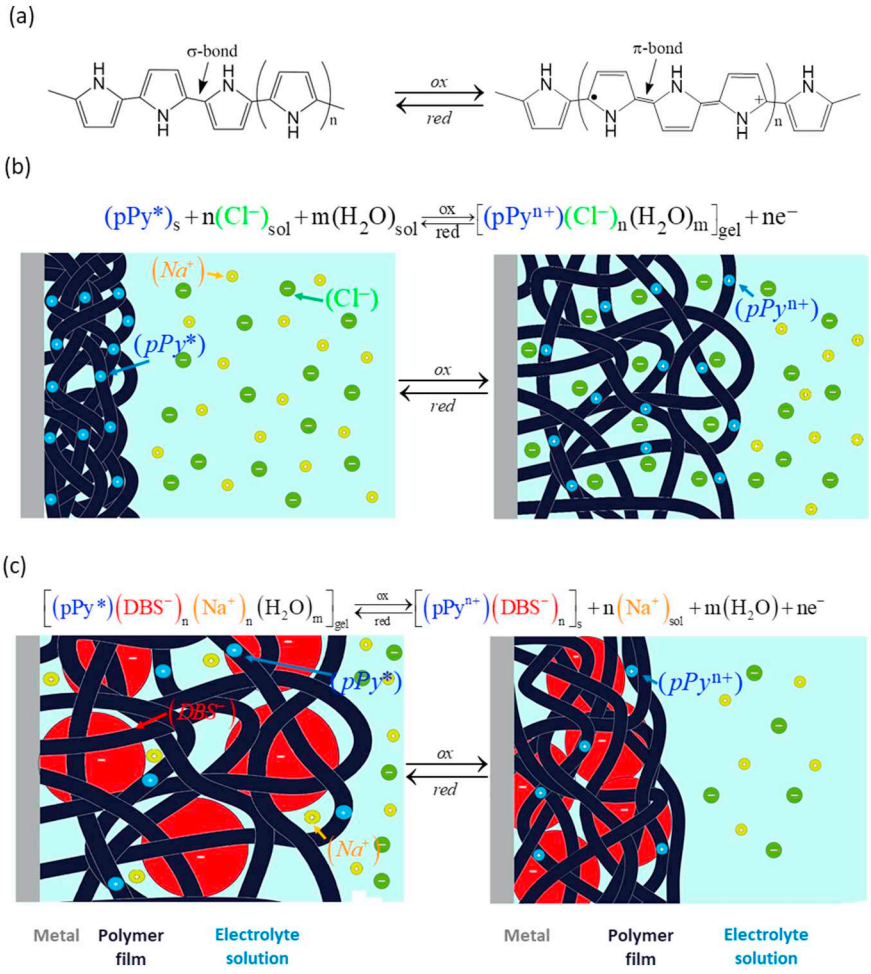

Fig. 1. (a) Reversible electrochemical oxidation/reduction of a single polypyrrole chain driving the exchange of σ bonds and π-conjugated structures between monomeric units by the extraction or injection of one electron. Polypyrrole multielectronic molecular motors in a polymeric film driven by *p*-doping processes (polypyrrole electrochemical oxidation/reduction): (b) with anion exchange causing film expansion/contraction, and (c) with cation exchange driving film contraction and expansion to maintain the charge and osmotic balance through the exchange of counterions and solvent molecules from the electrolyte.

every polypyrrole chain is the same in both material families (Fig. 1a), but the resulting macroscopic mechanical work is in the opposite direction: swelling (Fig. 1b) versus contraction (Fig. 1c) [5,26]. Here we will use polypyrrole films electrogenerated in the presence of sodium dodecylbenzene sulfonate (DBS), which will lead to the exchange of cations when the film is subjected to electrochemical control in an aqueous solution of NaCl [27,28]. We will use thin films covering a platinum plate to properly focus on their sensing properties, disregarding any parallel macroscopic actuation of the material found in thicker films. Thus, our goal here is to check if the reaction of polypyrrole molecular machines driven by *p*-doping processes with exchange of cations can sense any variation in the electrolyte concentration, similar to the previously developed electrochemical theoretical model for the exchange of anions in polypyrrole materials.

The parallel question should be how any biochemical molecular motor (i.e. actin-myosin-ATP in muscles or ionic channel proteins) can sense the working physicochemical conditions, whatever the ions (cations or anions) involved used to originate the actuation, as well as the origin of the nervous pulse that communicates quantitative information about these conditions to the brain.

2. Experimental

2.1. Chemicals

Pyrrole (Py) was purchased from Fluka, distilled under vacuum before use and stored at −10 °C. 4-Dodecylbenzenesulfonic acid (DBSA), mixture of isomers ≥95%, was obtained from Sigma Aldrich and was stored at −4 °C. Analytical reagent quality sodium chloride (NaCl) came from Panreac, and was used as received. All solutions were prepared using ultra-pure water from a Milli-Q equipment (18.2 MΩ cm).

2.2. Electrochemical equipment

An AUTOLAB/PGSTAT100 potentiostat-galvanostat was used to carry out the electrochemical procedures programmed in NOVA 1.11 using a three-electrode electrochemical cell. A commercial reference electrode (RE) of Ag/AgCl (3 M KCl) from CRISON was used. The working electrode (WE) was a platinum plate with a surface area of 1 cm^2 and the counter electrode (CE) was a 2 × 5 cm stainless-steel plate.

3. Results and discussion

3.1. Synthesis of PPy (DBS) films

The polypyrrole (DBS) films were electrogenerated galvanostatically [29,30] as thin films covering a Pt sheet using a flow of current density 2 mA cm^{-2} for 300 s on a clean Pt electrode (WE) with 1 cm^2 of total surface area submerged in fresh 0.1 M Py and 0.1 M DBSA aqueous solution at room temperature. The conditions were similar to those used to produce the anion-exchanging polypyrrole thin films on which the aforementioned theoretical model was based [19–21,31]. An example of a chronopotentiometric response obtained during the synthesis of a PPy (DBS) film is presented in Fig. S1 (in the Supplementary material). Every electrogenerated film was characterized before the series of experiments by checking its electroactivity in consecutive potential cycles between −0.8 and 0.5 V at a scan rate of 50 mVs^{-1} in 0.1 M NaCl aqueous solution. The potential range and scan rate were selected in order to clearly observe the redox peaks while avoiding a parallel degradative process of the thin film initiated by hydrogen or oxygen evolution [32]. Fig. S2a shows the stationary voltammetric responses and Fig. S2b the corresponding coulovoltammetric responses of the newly electrogenerated films. In the subsequent experiments these will be taken as the reference for the original electrochemical state of the material [19,33,34].

3.2. Effect of the electrolyte concentration: experimental methodology

The influence of the electrolyte concentration on the electrochemical responses of the PPy (DBS) films was studied under galvanostatic conditions, as described in previous works [21,22]. The material was subjected to a series of square current waves between +1.5 mA and −1.5 mA, each applied for 6 s (Fig. 2a). The procedure was repeated in different electrolyte concentrations: 0.025, 0.05, 0.075, 0.1, 0.5 and 0.75 M NaCl aqueous solutions.

Before and after each experiment with a different electrolyte concentration, the electroactivity of the film was checked by cyclic voltammetry in 0.1 M NaCl aqueous solution (control solution). Figs. S3a and S3b show, respectively, the voltammetric and coulovoltammetric controls. The control responses overlap, supporting the view that the electroactivity of the film remains constant over the experimental series and that the variations observed from the experimental responses can only be attributed to the influence of the electrolyte concentration. If the reversible charge obtained from the coulovoltammetric control dropped over 5% relative to that of the control before the experiment, the film was replaced by a newly synthesized one, repeating the study of the relevant electrolyte concentration.

3.3. Effect of the electrolyte concentration on the chronopotentiometric responses

All PPy (DBS) films were initially reduced for 6 s at −0.4 V. Then, three consecutive square waves of ± 1.5 mA, Fig. 2a, were applied to the material. Fig. 2b shows the consecutive chronopotentiograms obtained in two NaCl aqueous solutions (0.75 M and 0.025 M), the rest of the responses lying between them. After the second wave stationary responses are obtained, indicating that any initial structural memory had been deleted from the material during the first cycle.

Fig. 3a and b shows the beginning of the anodic and cathodic chronopotentiometric responses (between 0 and 3 s of current flow). The baseline (zero potential) for every response is the material potential at the beginning of each anodic, or cathodic, current step.

When film oxidation or reduction reactions occur in rising NaCl concentrations, the potential of the material evolves at decreasing anodic or cathodic potentials, respectively. The results are consistent with those obtained in previous works using PPy films (exchanging anions) in NaCl [31] or $LiClO_4$ [35–37], both being either a component of an artificial muscle or being supported on metal electrodes. Similar empirical results were obtained from thick PPy (DBS) films playing the role of bilayer PPy (DBS)/tape artificial muscles or as free-standing electrodes. In addition, the macroscopic volume variation of the films, which corresponds to a muscle movement, supports the concept of the PPy(DBS) shrinking/swelling by oxidation/reduction, respectively, as expected for a reaction-driven exchange of cations as described in Eq. (1) [30,38–43]. This means that for polypyrrole (DBS) exchanging cations with the electrolyte under oxidation/reduction conditions [44], the reaction adapts to the electrolyte concentration at any given reaction time. The reaction of the material can therefore be seen as a continuous sensor of the electrolyte concentration and the potential of the material represents the magnitude of the working chemical energy.

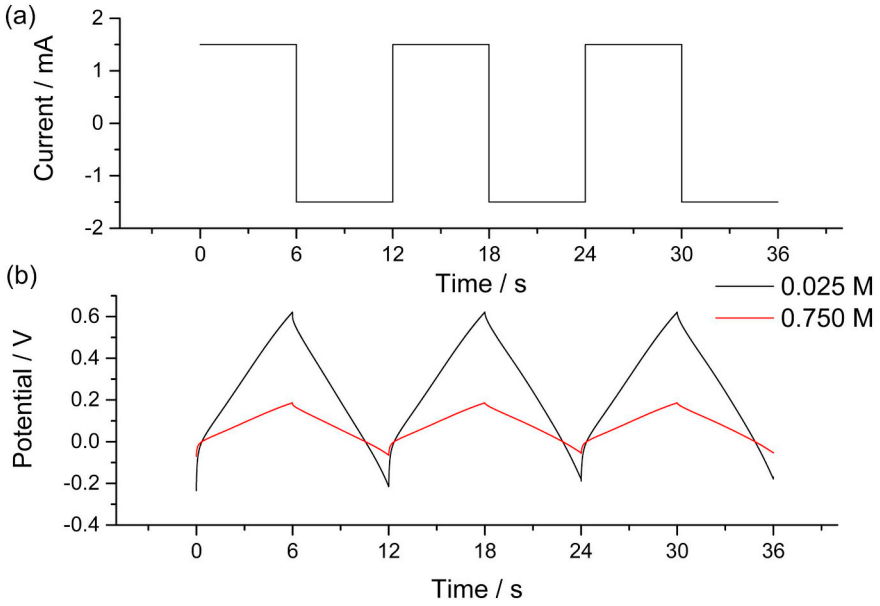

Fig. 2. (a) Successive square current waves between 1.5 mA and −1.5 mA, each of 6 s duration. (b) Chronopotentiograms obtained from a PPy (DBS) film in 0.75 M and 0.025 M NaCl aqueous solution.

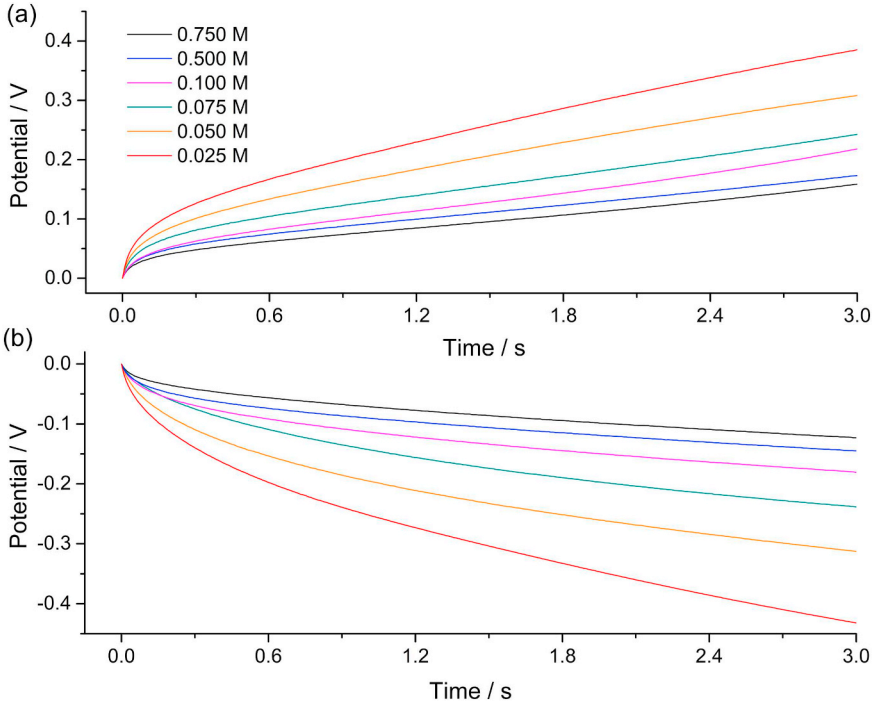

Fig. 3. Stationary chronopotentiometric responses obtained during (a) oxidation (+1.5 mA) and (b) reduction (−1.5 mA) of the PPy (DBS) film in NaCl aqueous solutions of various concentrations. Only the initial 3 s of current flow are presented here.

3.4. Theoretical description

The electrochemical reversible *p*-doping/*p*-dedoping (oxidation/reduction) reaction of the PPy(DBS) film drives the reversible exchange of cations [27,28]:

$$[(pPy^{*})(DBS^{-})_n(Na^{+})_n(H_2O)_m]_{gel} \underset{red}{\overset{ox}{\rightleftarrows}} [(pPy^{n+})(DBS^{-})_n]_s + n(Na^{+})_{sol} + m(H_2O) + ne^{-} \quad (1)$$

where PPy* represents the active centres on every polypyrrole chain in the film where a polaron, a radical cation (PPy^{+}), will be generated after the oxidation reaction; DBS^{-} represents the dodecylbenzene sulfonate anions incorporated in the film during the electrosynthesis of the polypyrrole in order to balance the positive charges on the electrogenerated and oxidized polypyrrole chains: these large anions cannot be exchanged with this electrolyte, remaining trapped in the film during the reactions [29]; Na^{+}, the sodium cations exchanged with the electrolyte for charge balance; n is the number of both electrons and sodium cations exchanged with the solution per polymeric chain; m is the number of solvent molecules (H_2O) exchanged to keep the osmotic balance (the film becomes a dense gel, subscript gel); s means solid and sol, solution.

These reversible reactions drive both the macroscopic structural and volumetric changes of the electroactive material and the conformational movements of each constituent chain, which becomes a molecular machine [38,45]. Oxidation of the film (Eq. (1)) drives film contraction (Fig. 1c) as shown by the macroscopic bending movement of bilayer (conducting polymer/tape) artificial muscles. Reduction of the film drives film swelling, due to the inclusion of cations and solvent [46].

The composition of the material (ions, solvent and chemical molecular motors) thus replicates, in a simplified form, the dense gel structure of the intracellular matrix (ICM) in functional cells.

3.5. Sensing principle under reactions

As reported in the literature, reactions involving molecular machines as reactants respond to any variation of energy conditions (mechanical, electrical, thermal or chemical), by adapting the consumed reaction energy according to the new energy conditions [14]. Alternatively, the reaction energy senses, instantaneously, any perturbation in the energy of its surroundings. Accordingly, any change in the physicochemical variables influencing the reaction rate should generate a change in the consumed energy (U). For the electrochemical reactions studied here, the reaction energy is the product of the material potential evolution during the reaction (E) and the consumed charge (Q).

3.6. The evolution of the material potential responds to the electrolyte concentration (chemical energy)

The theoretical model for electroactive materials exchanging *anions* describes the material potential evolution, $E(t)$, under the application of square current waves, as a function of the natural logarithm of the electrolyte concentration during the reaction time [21,22]. By applying the same theoretical model for electroactive materials exchanging *cations*:

$$E(t) = n_1 - m_1 \ln[Na^{+}] \quad (2)$$

where the meanings of the slope (m_1) and the intercept (n_1) are presented in the Supplementary material. Thus, starting every time from the same initial reduced state of the PPy (DBS) film, after a constant time (t) of anodic current (i) flow, the material potential should be a function of the natural logarithm of the electrolyte concentration. The plot of this function would result in a straight line, which acts as the calibration line of the sensor. These conditions mean that, whatever the concentration, the material potential is determined when the reacting material has the same polymer/counterion composition. Lower potentials are expected in rising electrolyte concentrations, which is corroborated by the experimental results (Fig. 4). The energy consumed by the reaction responds to electrolyte concentration changes.

As previously reported, the electrical energy $U(t)$ consumed by the oxidation/reduction reactions of conducting polymer films driving the exchange (injection/expulsion) of *anions* to convert the material between reduced and oxidized states (by consumption of the same

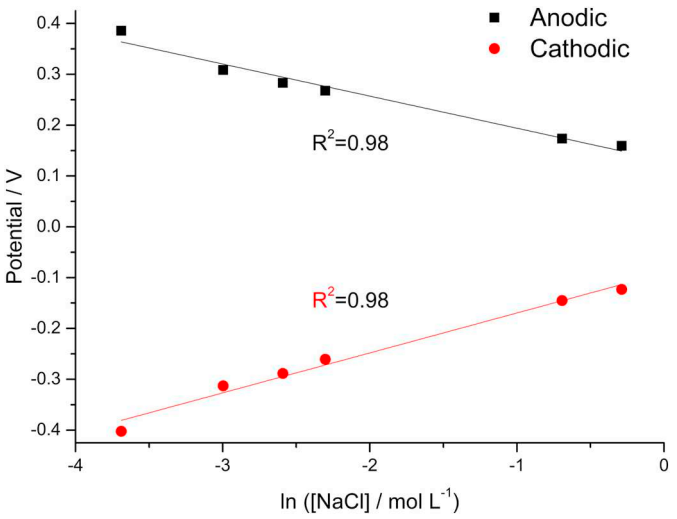

Fig. 4. Potential reached by the PPy (DBS)/Pt film vs the natural logarithm of each electrolyte concentration studied.

reaction charge) is also a function of the natural logarithm of the electrolyte concentration [21,22]. Now we will check the corresponding equation for films exchanging *cations* (Eq. (1)):

$$U(t) = n_2 - m_2 \ln[Na^+] \quad (3)$$

Under galvanostatic conditions, the evolution of the energy can be obtained experimentally by the product of the intensity of the applied current (i) and the integrated area of the chronopotentiograms from Fig. 3, following Eq. (4) [14,31]. The energy consumed by the electrochemical reactions of the material decreases with rising electrolyte concentrations. The results fit the sensing equation (Eq. (3)) – see Fig. 5. The Supplementary material presents the experimental values of the slope (m_2) and the intercept (n_2).

$$U(t) = i \int E dt \quad (4)$$

The electrical energy consumed by polymeric molecular machines driving the exchange of cations with the electrolyte to push the material between the same reduced and oxidized states every time (same compositions) decreases when the surrounding chemical energy (electrolyte concentration) increases. The energy can therefore be seen as a sensor of any fluctuation in chemical energy in the reaction environment. Eq. (3) is the sensing equation and Fig. 5 depicts the calibration lines for the oxidation and reduction of the material.

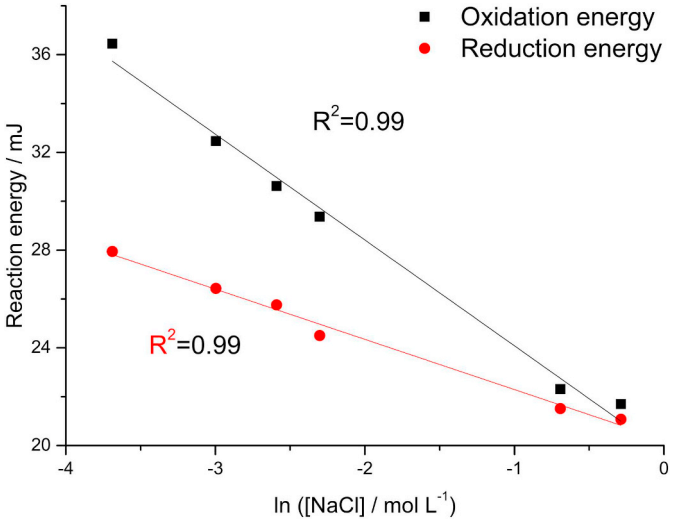

Fig. 5. Energy consumed by the PPy (DBS)/Pt film electrochemical reaction vs the natural logarithm of each electrolyte concentration studied.

As described for the reactions driving the exchange of anions, despite the symmetry of the reaction charges, the energy consumed during oxidation and reduction is quite different (energetic asymmetry) (Fig. 5). This fact can be attributed to the asymmetry of the reaction-driven structural changes [34]. Here, the energy consumed during polymer oxidation–shrinking is higher than that consumed during the reverse polymer reduction–swelling, regardless of the electrolyte concentration [20].

3.7. Biological interpretation

The origin of the nervesignals providing the brain with quantitative information about chemical (fatigue state) and physical (mechanical, thermal, and so on) muscle actuating conditions is still not well understood. Current research suggests that the muscular biochemical reaction (myosin-actin-ATP hydrolysis) is the origin of both the actuation of the molecular machines (actin-myosin) and the generation of nerve pulses [47,48].

The performance of ATP hydrolysis over actin and myosin gels in the laboratory, despite improvements in manipulating the actuation [6,7], is not sufficient to enable study of this issue. As an alternative, our group uses conducting polymers to replicate both the composition (molecular machines, ions and water) and the reactivity of the intracellular matrix (ICM) of muscle cells.

The experimental results support the view that the reaction energy of the model material instantaneously adapts to the reaction concentration. Translated to muscles, this should mean that the actin-myosin-ATP reaction energy adapts to the ATP concentration including, Eq. (3), quantitative information about the muscle fatigue state. A new hypothesis is shown for the origin of the sensing nerve pulses: the neuron terminals detect the reaction energy at any time during the muscular contraction and part of this energy generates a nervous pulse carrying this quantitative information to the brain. The brain is aware at all time of the effort required to perform the same muscular action under different fatigue (chemical) conditions. Under lower concentrations (i.e. after several muscular contractions) the reaction consumes more energy (Fig. 5) to drive the same actuation contraction.

In addition, natural muscles are analogous to asymmetric macroscopic chemical motors: they only work by muscle contraction. This means that their constituent molecular motors produce irreversible reactions. The question is why evolution has selected asymmetric molecular machines to perform some biological functions. Here, using artificial molecular machines, we have established that, despite reversible redox charges, the consumed energies are asymmetric (Fig. 4) due to the asymmetry in the energy of the conformational movements. Evolution has thus selected the most efficient method (from an energetic point of view) to perform biological functions.

Any electroactive materials containing molecular motors can now be used to quantify the effect of their surroundings on the energetic asymmetry of the corresponding reactions. The results can provide useful information as to how to develop artificial bifunctional tools (sensing-actuators) for applications ranging from the development of artificial muscles, smart membranes, and artificial synapses to constructing bio-replicating artificial robots.

4. Conclusions

During the reversible reaction of PPy (DBS) films submitted to square current waves in NaCl aqueous solutions, both the evolution of the material's potential and the reaction energy are a function of the natural logarithm of the electrolyte concentration: in effect, each reaction acts as a sensor of the local chemical energy conditions.

The same sensing behaviour is observed whether anions are exchanged (the film swells by oxidation) or cations are exchanged (the

film contracts by oxidation).

Only two connecting wires carry both the actuation order (current) and the sensing response (potential), replicating the communication between muscles and brain through only two (motor and sensory) neurons in animals.

In natural muscles, a fraction of the reaction energy may produce a nerve pulse to inform the brain about the state of muscle fatigue. After corroboration, this hypothesis could clarify the origin of nerve pulses and help to solve some correlated muscle malfunctions.

The corroborated empirical energetic asymmetry of reversible reactions involving molecular machines may lead to an improved understanding of the asymmetry of many biological functions.

Electroactive materials containing molecular motors can be considered as models of the intracellular matrix in functional cells. The influence of different reaction conditions gives quantitative information on similar biological functions driven by reactions involving molecular machines and thus how these can sometimes malfunction.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.elecom.2019.05.011.

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